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Study of the Effects of Annealing Temperature on the Properties of ZnO Thin Films Grown by Spray Pyrolysis Technique for Photovoltaic Applications

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Abstract: Zinc oxide (ZnO) thin films deposited on glass substrates at 300 °C by spray pyrolysis technique and then annealed at different temperatures ranging from 300 to 400 °C for 1 hour in air. The effects of the annealing temperature on the structural, optical and electrical properties of the ZnO thin films were studied. X-ray diffraction suggests that a hexagonal wurtzite structure with a strong (002) preferred orientation and the crystallite size increases with annealing temperature. The optical transmittance spectra showed transmittance higher about 82% in Vis and IR region of the annealed films at 375 °C. The direct optical band gap rises from 3.17 eV to 3.27 eV for as-deposited and annealed ZnO thin film at 375 °C, respectively. The resistivity values of the samples have changed from 6.27.10+2 to 7.50.10+1 (Ω.cm) with annealing temperature.

Keywords: Thin film, annealing temperature, spray pyrolysis, zinc oxide.

1 Introduction

Zinc oxide (ZnO) is a n-type compound semiconductor with a direct wide band gap [1]. It has a relatively large exciton binding energy (60 meV) at room temperature [2], good optical properties and a high stability [3]. Zinc oxide represents an important basic material due to its low cost as well as its electrical, optical and luminescent properties [4]. Overall, ZnO is of importance for fundamental research, and relevant for various fields of industrial and high technological applications such as gas sensors [5], optoelectronic [6], solar cell [7], UV light detector and Schottky diodes [8]. ZnO thin films have been prepared using various methods such as thermal evaporation [9], chemical vapor deposition [10], sol–gel method [11], electrochemically deposition, ion beam assisted deposition [12], rf magnetron sputtering deposition [13], metalorganic chemical vapor deposition [14] and spray pyrolysis aqueous solution method [15]. Among these methods, spray pyrolysis is especially suitable and particularly useful for large area applications, since it has proved to be a simple and inexpensive method.

In this work, we report the effect of annealing temperature on structural, optical and electrical properties of zinc oxide thin films prepared by spray pyrolysis technique.

2 Experimental Details

ZnO thin films were synthesized by the chemical spray technique on glass substrates at 300 °C (fig.1). After, the films were annealed at different temperatures from 300°C to 400 °C for 1h in air, in order to study the effect of the variation of the annealing temperature on the structural, optical and electrical properties of deposited films. The chemical precursor used is zinc chloride ($ZnCl_2$. H_2O), and it dissolved in double-distilled water at the 0.15 M concentration. Note that a small amount of hydrochloric acid (HCl) has been added to dissolve the zinc chloride since it gives a chemical precipitate if only double-distilled water is used to dissolve it. The substrates cleaned with acetone and double-distilled water. Furthermore, all the obtained films were manufactured under the same conditions summarized in Table.1.

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The structural characterization was performed at room temperature using a Bruker X-ray diffracto-meter model D2 Phaser with CuKα radiation (λ = 1.5406 Å). The optical transmittances have been recorded between 200 and 2500 nm wavelength using a JASCO 570 type UV-visible-NIR double-beam spectrophotometer. The electrical properties were measured by measuring ECOPIA HMS-5000 Hall Effect measurement system at room temperature.
17).

3 Results and Discussions

3.1 Structural Properties

The figure 2 shows the XRD diffraction spectra of ZnO thin films without and with annealing temperature at 300 °C to 400 °C. The obtained XRD spectra were analysed and compared with the standard card JCPDS (Joint Committee on Powder Diffraction Standards) N ° 36-1451 [16,17,18,19,20]. The deposited films are polycrystalline with hexagonal Wurtzite phase with a preferential orientation in the [002] direction indicating that the c-axis is perpendicular to the film surface.

By increasing the annealing temperature, the intensity of preferential orientation (002) was increased, which explain by coalescence of the crystallite of the films. These results are in good agreement with the calculated strain and crystallite size (Table 2). Indeed, it can be observed that the width at half maximum (FWHM) of the preferred orientation (002) peak of the films changes with increasing annealing temperature (see Table 2).

Table 1: Conditions for depositing of ZnO thin films annealed at different temperatures.

Chemical precursors	zinc chloride ($ZnCl_2$. H_2O)
Deposit temperature	300 °C± 10 °C
Annealing temperature	300 °C, 325 °C, 375 °C and 400 ± 10 °C
Distance between substrate and hotplate	30 cm
Spray solution flow rate	2 ml /min
volume of sprayed solution	50 ml

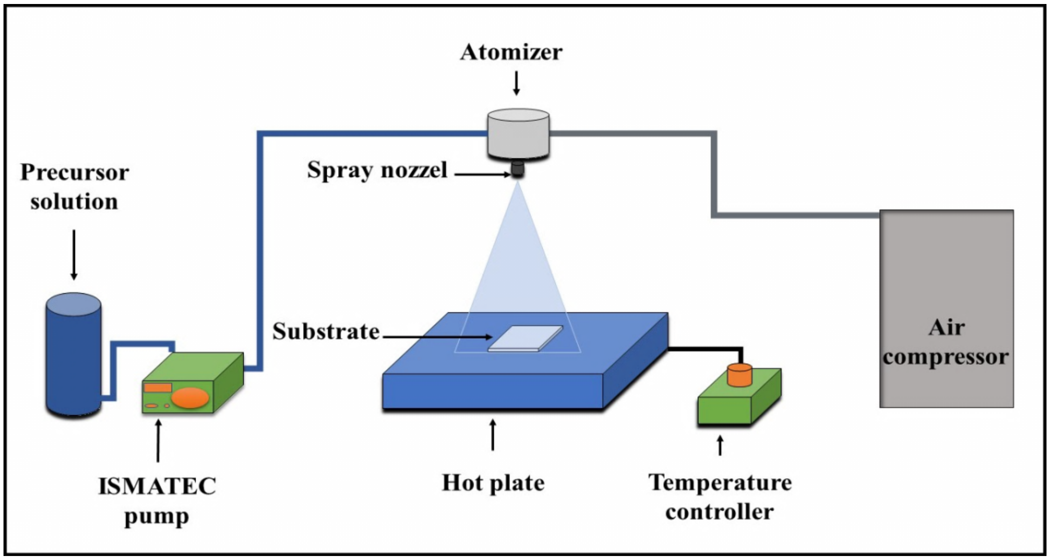


Fig.1: Schematic diagram of spray pyrolysis system used for the preparation of ZnO thin films.

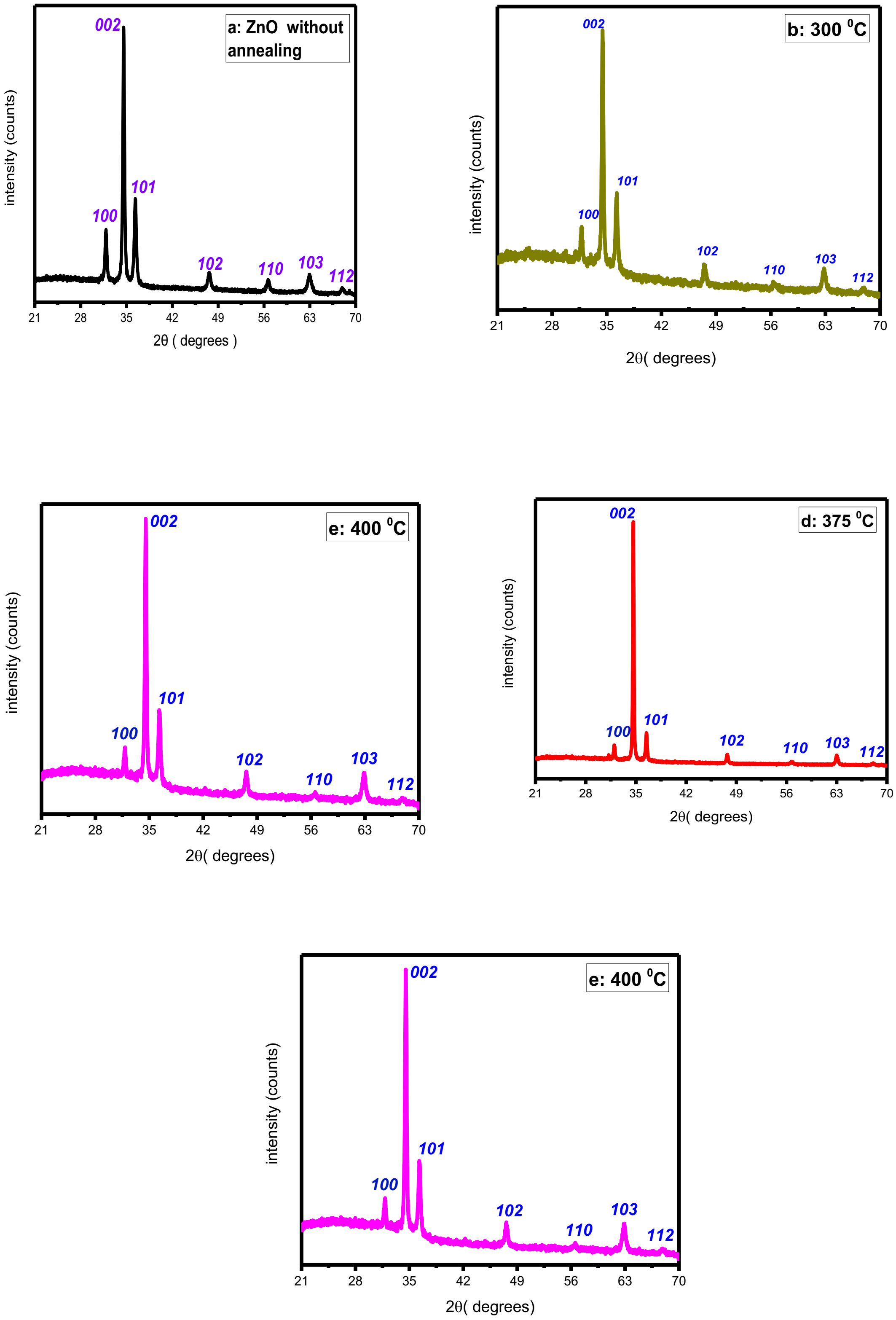


Fig 2: [a] without annealing [b] 300 °C [c] 325 °C [d] 375 °C [e] 400 °C.

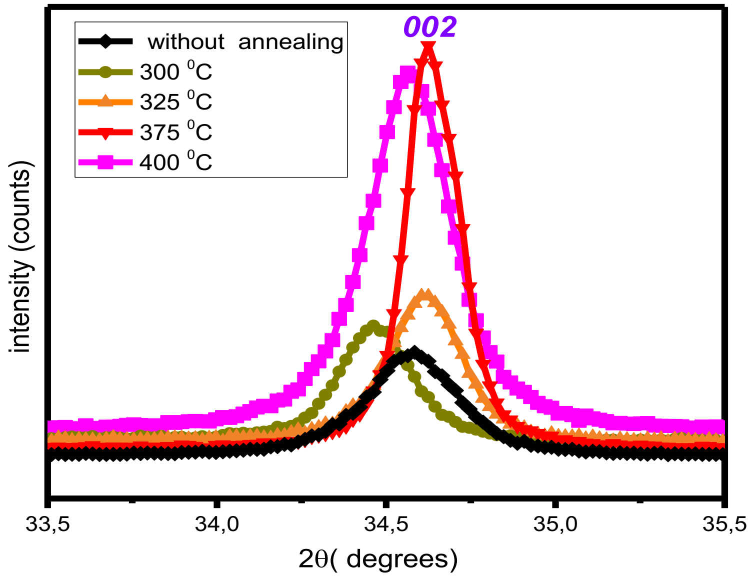


Fig 3: (002) peak position of the ZnO films for with and without annealing temperature.

The crystallite size of the films evaluated by Scherrer formula (1) [21,22]. The lattice constants, strains and dislocation density are also calculated and discussed.

$$D = \frac{k\lambda}{\beta \cos \theta} \qquad (1)$$

Where k=0.9, λ =1.5406, Å is the x-ray wavelength, β is the full width at half maximum (FWHM) of the XRD peak, and θ is Bragg's diffraction angle. The lattice parameters of the films have determined by the following relation [23,24]:

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \qquad (2)$$

The micro-strain (ε) and the dislocation density of the films estimated using the following formula [25,26]:

$$\varepsilon = \frac{\beta \cos \theta}{4} \qquad (3)$$

$$\delta = \frac{1}{D^2} \qquad (4)$$

All the obtained structural parameters including full width at half maximum (FWHM), crystallite sizes, lattice constants *(a* and *c*), strains and dislocation density are summarized in Table 2.

The obtained values ‘a’ and ‘c’ are 3.231 Å and 5.194 Å for pure ZnO. These values are in good agreement with JCPDS cards mentioned previously. The lattice parameters *a* and *c* of the films slightly change with annealing temperature which might be ascribed to effect of vacancies. Table indicates that (FWHM) values decreased with annealing temperature, this implies an increases in the average crystallite size (D) of the films from 38.98 to 42.30 indicating an improvement in the crystallinity of the films. The annealing temperature provides thermal energy to activate atom diffusion and hence, facilitate to repairing the dislocated atomic occupancies and even promote the coalescence of adjacent particles [23,24]. The annealing films exhibit less structural disorder that indicates an increase in the crystallinity of the films [24]. It is also observed from table1 that there is an inverse relationship between the crystallite size and structural disorder (strain and dislocation density), this explains that the stain and dislocation density contributes to the smash grain.

Table 2: Structural parameters of ZnO thin films annealed at different temperatures.

Samples	$2\theta^0$ (002)	FWHM $.10^{-3}$ (Degrees)	Crystallite size (nm)	a (A^0)	c (A^0)	Strain (10^{-4})	Dislocation density (10^{-4} Line/nm^2)
Without annealing	34.58	5.51	38.98	3.231	5.194	13.15	6.59
300°C	34.45	5.44	39.59	3.234	5.195	12.99	6.37
325°C	34.61	5.37	39.70	3.241	5.192	12.82	6.34
375°C	34.56	5.18	42.30	3.241	5.192	12.36	5.58
400°C	34.62	5.24	40.69	3.234	5.195	12.50	6.03

3.2 Optical properties

The optical transmittance spectrum as a function of the wavelength of the prepared ZnO thin films presented in Figure 4. All the grown films are highly transparent with an average transmission of 71-79 % in the visible and infrared region which is requested for satisfactory optical window in visible range in photovoltaic systems [25]. In addition, the deficiency of interference fringes in transmission spectra is due the surface roughness caused by the spray pyrolysis technique, which may be due to very small droplets resulting from this technique that vaporize above the glass substrates and condense as clusters [26]. It is also observed that a shift in the fundamental absorption edge of the films, this can be correlated to the variation in the optical band gap of the films (see Fig 5) with increasing annealing temperature.

The transmittance achieved 82 % for the films annealed at 375 °C (Fig.4.d), this improving can be due to a low scattering effects resulting from the structural homogeneity of the films and the apparent high crystallinity [27]. Thus, the XRD results corroborate well with the transmittance spectra.

The formula used to calculate the optical band gap energy of the films is [28]:

$$(\alpha h\nu)^n = A(h\nu - Eg) \qquad (5)$$

Where a: Absorption coefficient, $h\nu$: Photon energy, A: relation constant, Eg : optical band gap. For: n =2 direct band gap semiconductors and n = 0.5 indirect band gap semiconductors.

The optical band gap increases from 3.17 eV to 3.27 eV after annealed (Fig.5). The increase of band gap of the films due the oxygen diffusion with annealing temperature. The optical properties of the films generally influenced by the annealing temperature [29].

The Urbach energy estimated from the variation of the absorption coefficient. The absorption coefficient of the films shows a tail for the photon energy sub-band [28]:

$$\alpha = \alpha_0 \exp(\frac{h\nu}{E_U}) \qquad (6)$$

Where α_0 is a constant and E*u* the Urbach energy.

The Urbach energy found to decrease from 0.35 eV of the ZnO films without annealing to 0.26 eV of the annealed films at 375 °C (Table 3), which leads to decrease of disorder of the films [29]. This is consistent with the results from optical band gap (Table 2).

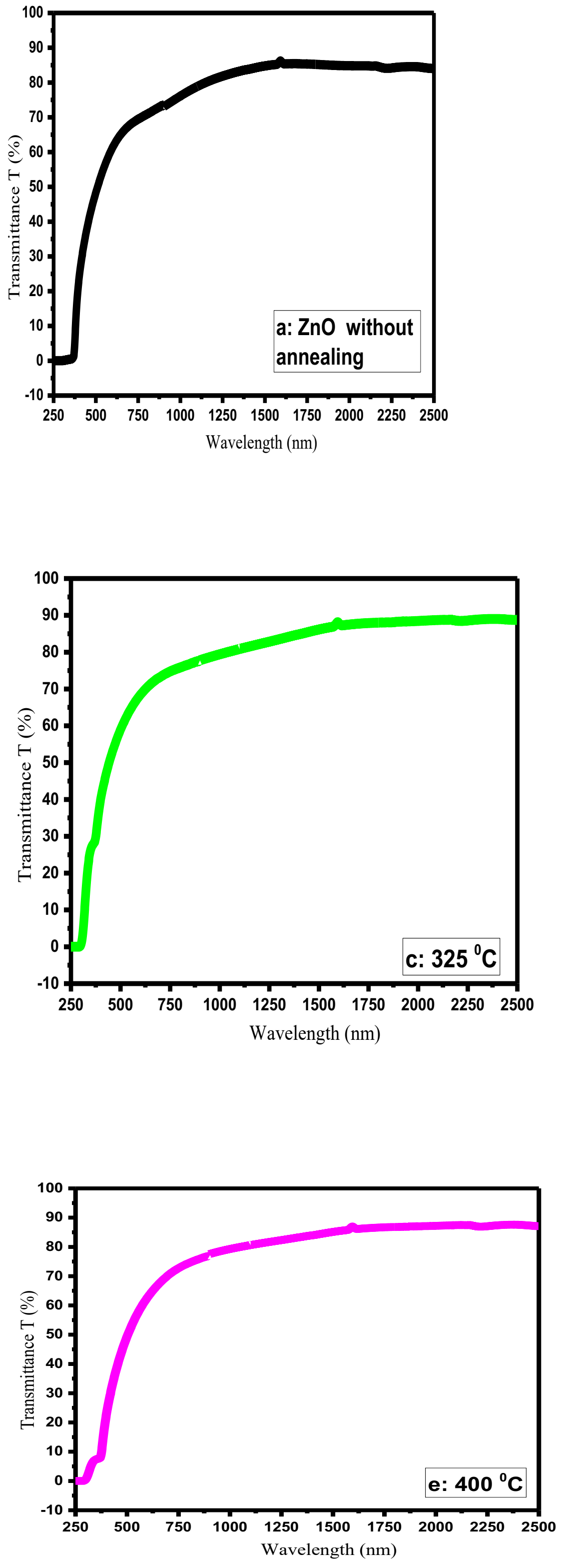
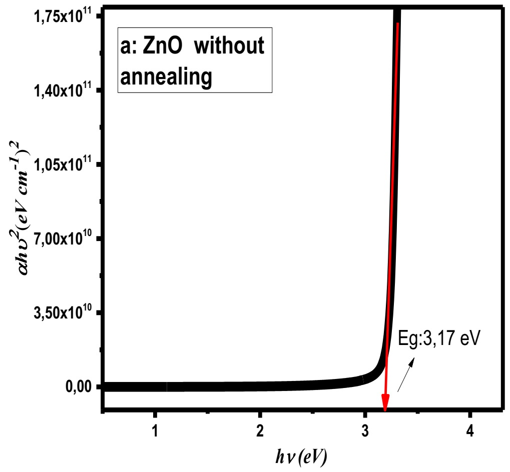
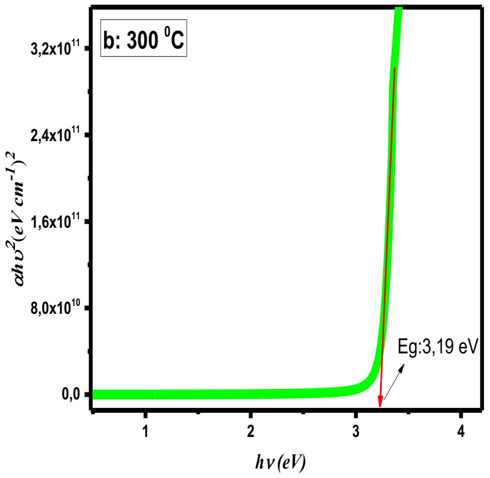


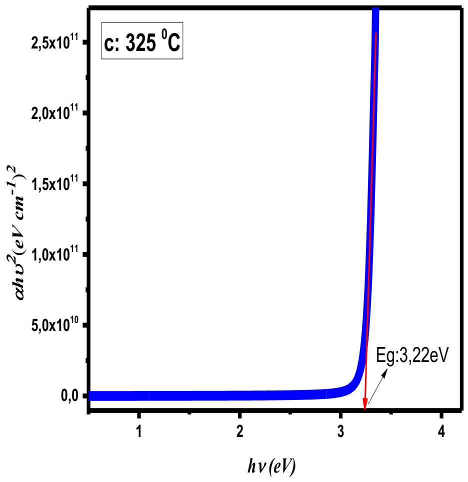
Fig 4: Transmittance spectra of ZnO thin films [a] without annealing [b] 300 °C [c] 325 °C [d] 375 °C [e] 400 °C.

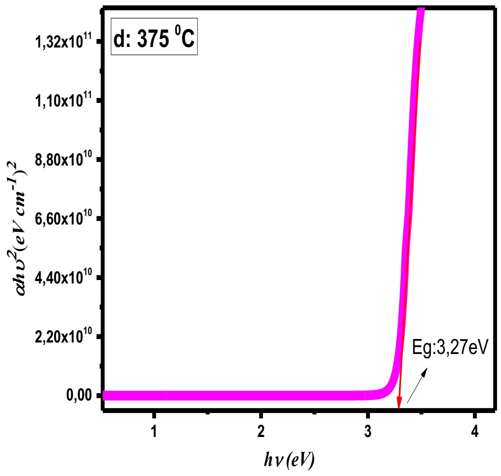
Table 3: Optical parameters of deposited thin films.

samples	Eg (eV)	Eu (eV)
Without annealing	3.17	0.35
300°C	3.19	0.31
325°C	3.22	0.29
375°C	3.27	0.26
400°C	3.26	0.27









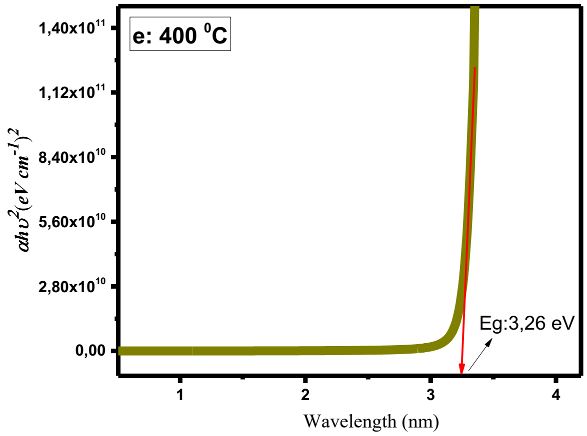


Fig 5: Variation of $(ahu)^2$ with photon energy of ZnO thin films [a] without annealing [b] 300 °C [c] 325 °C [d] 375 °C [e] 400 °C.

3.3 Electrical properties

The electrical resistivity decreased from $6.26.10^{+2}$ to $7.49.10^{+1}$ (Ω.cm) after annealing temperature (Table.4), which can be explained by increasing of the potential barriers, because the introduced atoms are segregated into the grain boundaries, this interpretation is consistent with the authors [30].

Table 4: Electrical parameters of prepared thin films.

Samples	Mobilité (cm²/VS)	Carrier Concentrations (cm⁻³)	Resistivity (Ω.cm)	Sheet Resistance (Rsh) (MΩ/sq)
Without annealing	3.43	$-2.90.10^{+15}$	$6.27.10^{+2}$	6.25
300°C	1.97	$-2.66.10^{+16}$	$1.20.10^{+2}$	1.19
325°C	3.14	$-5.58.10^{+16}$	$8.75.10^{+1}$	8.76
375°C	2.70	$-3.09.10^{+17}$	$7.50.10^{+1}$	7.49
400°C	1.74	$-1.63.10^{+16}$	$2.21.10^{+2}$	2.21

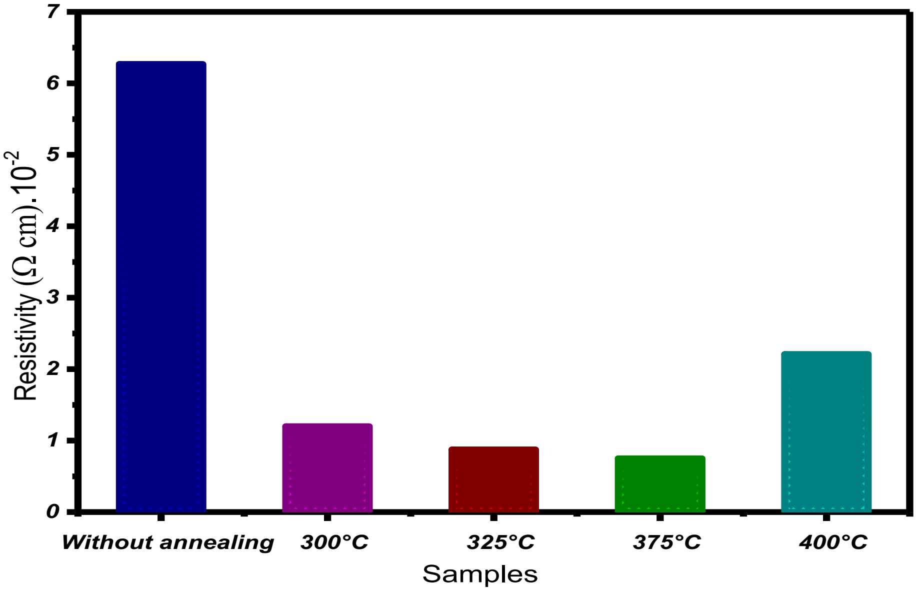


Fig. 6: Electrical resistivity variation of ZnO thin film annealed at different temperatures.

4 Conclusions

The ZnO thin films have been grown by spray pyrolysis method on glass substrates. The films are annealed at a temperature of 300 °C to 400 °C. The influence of annealing temperature on structural, optical and electrical properties was investigated. The XRD results reveal that the deposited thin film has a good polycrystalline hexagonal wurtzite structure with a strong (002) preferred orientation. The crystalline size rises to 42.3 nm with annealing temperature of 375°C. The average transmittance in visible and IR region reach 82 % with annealing temperature of 375°C. The band gap energy varies from 3.17 to 3.27 eV for the without to annealed ZnO thin film at 375 °C, respectively. The electrical resistivity measured of our films in the order $7.50.10^{+1}$ (Ω.cm). The experimental results revealed than ZnO films annealed at 375°C exhibit excellent crystalline structure, good transmittance and low resistivity than other annealing temperatures, suggesting that this temperature is the preferable one for candidate for optoelectronic applications such as photovoltaic solar cells.

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